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(54) LIGHT SENSITIVE COMPOSITION

(71) We, SHIPLEY COMPANY INC., a Corporation organized and existing under the laws of the State of Massachusetts, United States of America, of 2300 Washington Street, Newton, Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvement in and relating to photosensitive compositions.

As is known in the art, photosensitive resists are thin coatings (typically less than one half mil) produced from solutions which when exposed to light of the appropriate wave length, are chemically changed with regard to their solubility to certain solvents (developers). Two types of resist are available, *viz* negative-acting and positive acting. The negative-acting resist is a mixture which is initially soluble in its developer but which after exposure to light becomes insoluble in the developer. Exposure is affected through a film pattern and the unexposed resist is selectively dissolved, softened or washed away leaving the desired resist pattern on a laminate. Positive-acting resists work in the opposite fashion, exposure to light making the resist soluble in the developer. The resist pattern that remains after development (and post-baking in some cases) is insoluble and chemically resistant to the solutions used in conjunction with photoresists.

Typical examples of photosensitive materials used for resist formulations include vinyl cinnamate copolymers, acetophenone and cinnamate quaternary salts, benzyl acetophenone, and various diazide compounds as disclosed in U.S. Patents Numbers 3,046,118; 3,106,465 and 3,148,983.

Because of the high cost of the light sensitive materials used for such resists, it has been the practice in the art to mix film-forming resins with the light sensitive materials not only to lower the cost of the resist, but also to provide flexible films having more desirable physical properties.

The film-forming resins reduce the concentration of the light sensitive material in the light sensitive coatings typically by as much as 50% or somewhat more and thereby reduce the cost of the light sensitive formulation.

It is also known in the art to add alkali soluble Novolak-type phenolic or epoxy resins resistant to strong inorganic acids as listed in Karsten's (Lachrohstoff-Tabellene) Tables of Starting Materials for Lacquers, Second Edition, 1959, page 106.

The present invention is concerned with photoresist compositions comprising a light sensitive diazide compound and a resin component. The term "light sensitive diazide compound" as used herein is intended to refer to a compound containing a diazide grouping (i.e. a group $=N_2$ directly attached to a carbon atom) and which on exposure to light of the appropriate wavelength, undergoes a chemical change and is converted to a product having different solubility characteristics from the unirradiated compound. Thus the present invention is concerned with photoresist compositions comprising a light sensitive diazide compound and a resin which are either rendered soluble to a developer (positive working) or insoluble to a developer on exposure to light of the appropriate wavelength.

In accordance with the present invention, it has been discovered that a light sensitive coating can be provided that has a low content of light sensitive diazide material, i.e. between 2 and 20% and, preferably between 8 and 12% of the total solids, by incorporating in the coating composition a non-crosslinked carboxyl group containing acrylic polymer. In addition, the coating has excellent physical and chemical properties, at least comparable with prior art light sensitive coatings and in many instances improved over the prior art. Thus for example, relatively thick coatings can be formed, i.e. one mil or thicker, which coatings have exposure speeds equivalent to the thinner coatings of the prior art and developability characteristics permitting rapid

development of images having excellent image resolution. Thus it is a discovery of this invention that due to the use of the non-cross-linked acrylic resin the concentration of the light-sensitive material in the photoresist coating may be substantially reduced and in fact, a high concentration such as 50% by weight or more, of light-sensitive material is actually detrimental.

According to the invention there is provided a photoresist composition comprising a light sensitive diazide compound (as hereinbefore defined) together with a non-cross-linked carboxyl group-containing acrylic resin alone, the said acrylic resin together with another resin other than a novolak resin (the acrylic resin forming more than 50% by weight of the resin component), or the said acrylic resin together with a novolak resin (the novolak resin forming 1 to 90% by weight of the resin component) and in which the composition contains between 2 and 20% by weight of light sensitive diazide compound. The acrylic resin used is preferably a terpolymer of three monomers including an acrylic acid as one monomer.

The acrylic resins which may be used in the compositions of the invention are acrylic resins which are well known in the art and described in numerous publications including, for example, the *Modern Plastics Encyclopedia for 1968,* Volume 45, number 14A, McGraw-Hill Publications, pages 136 to 138. In general, the acrylic resins are polymers or copolymers of acrylic acid or methacrylic acid and copolymers of esters of these acids or acrylonitrile. Acrylonitrile and the methyl and ethyl esters of acrylic and methacrylic acid are the most frequently used starting materials, it being understood that a free carboxyl group-containing monomer must form one starting material. These colourless liquid monomer esters polymerize readily in the presence of light, heat or catalysts such as benzoyl peroxide to give higher molecular weight polymers.

For the purposes of the present invention, the resins known in the art as the "carboxyl type cross-linkable with epoxy resins" are preferred. Resins identified in this manner are described in the publication *Acryloid Thermosetting Acrylic Resins* Rohm and Haas Company, Philadelphia, Pennsylvania, August, 1968.

The most preferred acrylic resins are terpolymers formed by the terpolymerization of three monomers for example methyl acrylate, styrene and acrylic acid. These terpolymers suitably contain carboxyl groups (—COOH) in the range of from 3 to 15% by weight. This has been found to be a desirable range for both the terpolymer and other acrylic resins for use in this invention since photoresists formulated with resins that contain more than 15% of carboxyl groups are either over developed or have unsatisfactory etch resistance and with less than 3% of carboxyl groups, incomplete development may occur.

As will be readily apparent from the above discussion, the key chemical moiety in the terpolymer resin appears to be the carboxyl grouping introduced by means of acrylic acid, methacrylic acid or maleic acid monomer. The ratio of the concentration of the other two monomers can be varied over a wide range. Furthermore, other monomers may be substituted for both the methyl acrylate and styrene without noticeable detrimental effects. For example, alkyl acrylates such as ethyl acrylate and propyl acrylate may be used to replace the methyl acrylate monomer. With regard to the styrene monomer, other monomers such as *p* - methyl styrene, *p* - chloro styrene and ethylstyrene may be substituted without any resultant detrimental effects. In any event the monomer mixture must contain a monomer having a free carboxyl group.

A preferred terpolymer for use in the compositions of the invention is one which is comprised of 57.5% ethyl acrylate, 32.6% styrene and 9.9% acrylic acid. A terpolymer of this type is commercially available from the Rohm and Haas Company under the tradename "Acryloid AT-70".

The acrylic resins provide additional advantages besides the cost savings resulting from decrease in the quantity of the photosensitive material. For example, a photosensitive layer formed from the preferred composition of this invention requires a substantially shorter exposure to light than a photosensitive layer of the prior art of the same thickness. Alternatively, thicker coatings may be formed from the photosensitive materials of this invention without increasing the required exposure time beyond that required for prior art photosensitive layers.

In addition, the photosensitive compositions of this invention provide photosensitive coatings having good film properties such as good flexibility, improved bonding to a substrate, excellent resistance to solvents and other chemicals, toughness and good dielectric properties. These film properties are believed to be due in part to the decreased concentration of light sensitive material which acts as a contaminant with respect to the film properties. An additional advantage to the use of the acrylic resins, particularly the preferred terpolymers described above, is better edge acuity upon development of these photosensitive materials thereby resulting in sharper images. Other advantages include better adhesion to substrates and improved storage life to use.

The photosensitive coatings may comprise only the light sensitive material and the acrylic resin, but preferably comprises the light sensitive material in a resin system containing the acrylic resin as a key ingredient. In this re-

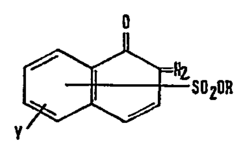
gard, other resins may be added to the resin system for specific film properties. Resins typically added to photoresists include the cellulose ethers, polyesters, polyvinyl alcohols, polyvinyl acetals, phenol-formaldehyde resins, melamine - formaldehyde resins, styrene resins, epoxy resins, phenol - furfural resins and polyurethanes.

In the most preferred embodiment of this invention, the acrylic resin is used in combination with a novolak resin, such as a phenol-formaldehyde resin, as this combination of resins provides the most desirable film properties. In combination with the novolak resin, the acrylic resin may be used in minor amounts even though it is a key ingredient.

Thus the concentration of the novolak varies from 1 to 90% by weight of the total weight of resin, but preferably varies from 25 to 75% by weight and most preferably is from 40 to 60% by weight of the total weight of resin. It should be understood that other resins such as those noted above, and other additives such as plasticizers, and dyes in minor amounts, may be added to the resin component. Where the resin component comprises the acrylic resin and a secondary resin other than the novolak resin the acrylic resin forms more than 50% by weight of the total weight of resin.

The light sensitive materials used in the invention are diazide compounds well known in the art. A concise, but thorough discussion of these materials appears in *Light Sensitive Systems* Kosar, John Wiley and Sons, Incorporated, New York, 1965, pages 336 to 352.

Preferred diazide compounds are the light sensitive orthoquinone diazides, especially the ortho - quinone diazide sulphonic sulphonic acid esters represented by the following formula:



in which Y is hydrogen or halogen and R is a substituted or unsubstituted aryl or heterocyclic radical. Examples of materials conforming to the above general structure are set forth in U.S. Patent Number 3,046,121. Examples of other light sensitive diazide materials which may be used in accordance with this invention are set forth in the aforesaid *Light Sensitive Systems* and in U.S. Patents Numbers 3,046,121; 3,102,809; 3,106,465; 3,130,047; 3,130,048; 3,148,983, 3,061,430; 3,184,310; 3,188,210 and 3,201,239.

The light sensitive formulations of this invention are used in a conventional manner and are preferably applied to the substrate in the form of a solution containing the dissolved acrylic resin, the secondary resin and other additives, especially the novolak, and the light sensitive material. After application of the coating, it is dried preferably in an oven, and, depending upon the acrylic resin used, may be baked at mild temperatures of from about 150° to 200°F for a short time, typically less than 30 minutes, to cure the polymer. It is then exposed to light for from 1 to 20 minutes depending upon the formulation of the light sensitive layer, its thickness and the intensity of the light source. Thereafter, it is developed by contact with a suitable developer for a period of from 1 to 10 minutes, again dependent upon the formulation of both the coating and developer and the film thickness.

Where the light sensitive material is to be used as a photoresist, the metal support, in the portions bared by the developer is treated with a suitable etching solution for a time sufficient to etch the metal base to the desired degree. After etching, the plate is rinsed and the remaining light sensitive coating is removed, if desired, for example by treatment with organic solvents such as one of those disclosed above as useful in the preparation of the light sensitive coatings.

Where the acrylic resin comprises the predominant part of the resin system, prior art alkali developers are not suitable as they attack the exposed portions of the resist and are slow. A better developer comprises an aqueous solution of a compound containing both hydroxy and amine groups, such as the alkanolamines or solutions containing both amines and alcohols. Alkyl primary amines and polyhydroxy alcohols are preferred. The total active components in solution preferably comprise from about 2 to 25% by weight of the solution. A typical developer formulation comprises from 5 to 25% by volume of ethanolamine in water. Where the resin system comprises a high portion of the novolak resin, then the prior art alkali metal hydroxide solutions may be used. Depending upon the ratio of the acrylic resin to the novolak resin, the alkali metal hydroxide can be used in conjunction with the amine - hydroxide type developer as would be obvious to those skilled in the art.

In order that the invention may be well understood the following Examples are given by way of illustration only.

Example 1

A solution was prepared comprising 100 ml of glycol monoethyl ether, 3.3 grams of a photosensitive compound believed to be the 1,2 - naphthoquinone diazide - 5 - sulphonic acid ester of p - cumyl phenol and 50.7 grams of an acrylic resin terpolymer identified as Acryloid AT-70 of Rohm and Haas Company. This acrylic resin is sold in the form

of a solution of 50% resin in a xylene cellosolve acetate solvent (The word "Cellosolve" is a Registered Trade Mark). It has an acid equivalent of 875 and a viscosity of about 1200 to 2500 cps at 25°C. The solution so formed was coated onto one side of a copper clad laminate by means of a plate-roller after which the coating was dried and cured by placing the laminate in an oven maintained at about 200°F for about 10 minutes. The dried coating had a thickness of about 1.0 mil. The light sensitive layer of the photoresist was then exposed to a light source comprising a 10 amp arc lamp for a period of about 12 minutes under a negative pattern or master. The exposed layer was developed by washing with an aqueous solution containing 5 grams of butylamine and 5 ml of dibutyl alcohol for about 3 minutes. The developed image was of good resolution.

Example 2

The procedure of Example 1 was repeated, but Acryloid AT-101 was substituted for the Acryloid AT-70. The Acryloid AT-101 was obtained from Rohm and Haas Company and is a carboxyl group-containing, thermosetting acrylic resin believed to be essentially a homopolymer of methacrylic acid having a Brookfield viscosity of from 700 to 1300 cps at 25°C. Similar results were obtained.

Example 3

A commercially available photoresist identified as GAF photoresist Number 102 (a product of General Aniline and Film Corporation believed to comprise about 1 part 3 - diazo - 2,4 - diphenyl - 3H - pyrrolenine and about 3 parts of a mixture of polyvinyl acetate and a copolymer of vinyl acetate and crotonic acid in a ketone solvent) was mixed with the AT-70 acrylic resin of Example 1. Three parts by weight of the acrylic resin were added for each part of the GAF photoresist on a solids basis. Therefore, the total concentration of the diazo compound and the photoresist was one part by weight per 15 parts of polymer.

The photoresist so prepared was coated onto one side of a copper clad laminate by means of a plate-whirler, after which the coating was dried and cured by placing the laminate in an oven maintained at 150°F for about 15 minutes. The light sensitive layer of photoresist was then exposed to a light source comprising a 10 amp arc lamp for a period of about 5 minutes under a negative pattern or master. The exposed layer was developed with a solution containing 25% by volume ethanolamine. The photoresist was removed from the non-irradiated areas, but the photodecomposition products were left intact with the irradiated portions in a sharp image pattern.

Examples 4 to 8

Five solutions were prepared, each in 200 ml of glycol monoethyl ether. The formulations were as follows:

Example No.	Acrylic (1) resin (gm)	Novolak (2) resin (gm)	Photosensitizer (3) (gm)
4	80	20	10
5	60	40	10
6	50	50	10
7	40	60	10
8	20	80	10

(1) Acryloid AT-70 described above.
(2) Alnovol 429K, an alkali soluble phenol-formaldehyde novolak resin.
(3) The 1,2 - naphthoquinone diazide - 5 - sulphonic acid ester of *p* - cumyl phenol.

Each solution was coated onto one side of a copper clad laminate by means of a plate whirler after which the coating was dried and cured by placing the laminate in a oven maintained at about 200°F for about 10 minutes. The dried coatings had thicknesses varying from about 1.2 mils to about 1.8 mils. The light sensitive layers of photoresist were then exposed to a light source comprising a 10 amp arc light for a period of about 15 minutes under a negative pattern or master. Examples 4 and 5 were developed with a 10% by volume solution of ethanolamine, Examples 7 and 8 were developed with a 2% by weight solution of sodium hydroxide and Example 6 was developed with a solution of ethanolamine containing sodium hydroxide. In all cases, developed images were of excellent image pattern. Edge acuity of the developed images were excellent and the resist patterns were etch resistant, flexible and otherwise possessed good properties.

Example 9

A photoresist formulation was prepared having the following composition:

	grams
Photosensitizer(1)	4
acrylic resin(1)	70
epoxy resin(2)	30
methyl cellosolve acetate	400

(1) As in example 1
(2) The epoxy resin was Epon 1001, a medium molecular weight polymer formed from epichlorohydrin and Bisphenol A.

The photoresist was coated onto one side of a copper clad laminate by means of a plate-whirler and the coating was dried in an air circulating oven maintained at 150°F. The light sensitive layer was exposed to a negative image pattern through a light source comprising a 10 amp arc lamp for a period of about 6 minutes. The exposed laminate was developed with a developer comprising 5 grams of each of N - butylamine and ethanol in 1 liter of water. The developed image was of excellent definition.

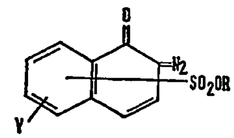
WHAT WE CLAIM IS:—

1. A photoresist composition comprising a light sensitive diazide compound (as hereinbefore defined) together with a non-cross-linked carboxyl group-containing acrylic resin alone, the said acrylic resin together with another resin other than a novolak resin (the acrylic resin forming more than 50% by weight of the resin component), or the said acrylic resin together with a novolak resin (the novolak resin forming 1 to 90% by weight of the resin component) and in which the composition contains between 2 and 20% by weight of light sensitive diazide compound.

2. A composition as claimed in claim 1 in which the light sensitive material forms from 8 to 12% by weight of the photoresist composition on a dry solids basis.

3. A composition as claimed in claim 1 or claim 2 in which the light sensitive material comprises one or more ortho-quinone diazides.

4. A composition as claimed in claim 3 in which the light sensitive material conforms to the formula:



in which Y is a hydrogen or halogen atom and R is a substituted or unsubstituted aryl or heterocyclic radical.

5. A composition as claimed in any one of the preceding claims in which the acrylic resin contains carboxyl groups in an amount of from 3 to 15% by weight of the resin.

6. A composition as claimed in any one of the preceding claims in which the acrylic resin is a terpolymer of three monomers, one of which is from acrylic acid, methacrylic acid or maleic acid.

7. A composition as claimed in claim 6 in which the acrylic resin is a terpolymer derived from (a) methyl acrylate, ethyl acrylate, or propyl acrylate, (b) *p* - methyl styrene, *p* - chloro styrene, *p* - ethyl styrene or styrene, and (c) acrylic acid, methacrylic acid or maleic acid; component (c) being present in an amount such that the carboxylic acid group content of the third monomer forms from 3 to 15% of the total weight of the three monomers.

8. A composition as claimed in any one of the preceding claims in which the novolak resin is of the phenol - formaldehyde type and forms from 25 to 75% by weight of the said resin component.

9. A composition as claimed in claim 8 in which the novolak resin forms from 40 to 60% by weight of said resin component.

10. A composition as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

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